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COMMITTEE OF EXPERTS ON THE
TRANSPORT OF DANGEROUS GOODS

REPORT OF THE COMMITTEE OF EXPERTS ON ITS NINETEENTH SESSION (2-10 December 1996)

ADDENDUM 4

Annex 6

Report on the work of the joint ILO/UN working groups on harmonised classification criteria for flammability and reactivity

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ANNEX 6

Report on the work of the joint ILO/UN working groups on harmonised classification criteria for flammability and reactivity

INTRODUCTION

1. In Rio de Janeiro in 1992 the United Nations Conference on the Environment and Development (UNCED) adopted, inter alia, Agenda 21, Chapter 19. This chapter concerns the environmentally sound management of toxic chemicals, including prevention of illegal international traffic in toxic and dangerous products, and contains Programme Area B, the objectives of which are the availibility, if feasible, by the year 2000, of a globally harmonized system of hazard classification and compatible labelling of chemicals. The globally harmonized system of classification should be used for all classification purposes whatever the regulatory context may be (safe use of dangerous substances at the workplace or at the home; safe handling or transport; protection of the environment; etc.).

2. Following that decision, international organisations and fora concerned decided to group the different criteria and to establish focal points to develop proposals for harmonised criteria on the basis of existing classification systems and existing sets of criteria.

3. For physico-chemical hazards, the International Labour Office (ILO) and the United Nations Economic and Social Council's Committee of Experts on the Transport of Dangerous Goods agreed to form two joint working groups in December 1994, one for criteria for reactivity of substances and one for criteria for flammability of substances.

4. In accordance with the UN Economic and Social Council's resolution 1995/6, both working groups held three sessions in July 1995, December 1995 and in July 1996. All delegations represented in the Committee of Experts on the Transport of Dangerous Goods and representatives from ILO took part in the work. The working groups concentrated on hazard levels, classification criteria and testing methods for the different hazard categories and criteria. Existing internationally recognized classification regimes and sets of criteria for the various types of protection were taken into account.

5. The reports of the working groups on each session were circulated by the United Nations secretariat respectively in documents ST/SG/AC.10/C.3/20/Add.2, ST/SG/AC.10/C.3/22/Add.2 and ST/SG/AC.10/C.3/24/Add.3.

WORKING GROUP ON HARMONIZED CLASSIFICATION CRITERIA FOR FLAMMABILITY

Scope of work

6. The work covered definitions, testing methods and criteria for flammable solids, flammable liquids, flammable gases and for the flammable properties of aerosols. The working group, chaired by Mr. G. Oberreuter (Germany), defined suitable sets of hazard levels for each criterion, taking into account the risks and danger potential in all areas of use of these classes of dangerous substances.

7. In some cases, it was discovered that certain dangerous substances or groups of substances exist, which are regarded as presenting a certain hazard by experience and expert judgement on a case by case basis, but which do not fit the defined criteria for the general dangerous properties of substances.

8. For gases, the UN Recommendations on the Transport of Dangerous Goods contains definitions of the physical state, e.g. refrigerated, liquefied; these are used to determine suitable transport conditions. It is suggested that there is no need to use such definitions for classification in other regulatory systems.

Results

9. After three sessions, the working group agreed by consensus on definitions to distinguish between solids, liquids and gases, and on the hazard levels and the correlated sets of criteria and cut-off values, as listed in annexed Tables 1 to 4. All criteria and values are based on existing and internationally accepted test methods, as indicated in the annexed tables. They may be applied, in the same manner, to pure substances as well as to mixtures and solutions such as formulations, preparations and wastes, according to the physical state (liquid, solid or gaseous) as indicated in the tables.

10. Further work is needed on the definition and the criteria for the flammable properties of aerosols (Table 5 to be completed).

WORKING GROUP ON HARMONIZED CLASSIFICATION CRITERIA FOR REACTIVITY

Scope of work

11. This work covered the remaining physico-chemical classification criteria not dealt with by the working group on harmonized classification criteria for flammability. This meant focusing on the definitions, test methods and criteria for explosive properties, organic peroxides, oxidisers, pyrophoricity, ability to self-heat, self-reactive and related substances, special groups of substances like desensitized explosives, ammonium nitrate and ammonium nitrate fertilizers as well as substances which emit toxic and flammable gases when in contact with water. The working group was chaired by Mr. R. Woodward (United Kingdom).

Results

12. At the end of the third session tables were devised, in line with those produced by the flammability working group on harmonized classification criteria for flammability, setting out the consensus reached on hazard categories, tests and criteria (see annexed Tables 6 and 7). They may be applied, in the same manner, to pure substances as well as to mixtures and solutions such as formulations, preparations and wastes, according to the physical state (liquid, solid or gaseous), as indicated in the tables.

13. The tables also indicate a number of issues upon which it was not possible to reach a consensus. This was either due to lack of time to complete the discussion or in some cases where the divergence of views from delegations required further thought to be given to the formulation of proposals for harmonization. The results set out in the tables, none the less, indicate a good deal of progress and some cause for optimism that, with further work, a more complete set of criteria can be produced.

PROPOSALS

14. Tables 1 to 7 contain proposals for definitions, classification criteria and cut off values for the hazards relating to the properties dealt with under flammability and reactivity where consensus has been reached. They also identify the areas where consensus was not forthcoming and where further work will be needed.

15. The Committee of Experts on the Transport of Dangerous Goods at its nineteenth session (2-10 December 1996) took note of the progress made so far and agreed with the proposals where consensus had been reached. The Committee agreed that the work should be pursued in 1997 to solve the remaining issues as indicated in this report.

16. The Committee agreed that this report and the proposals should be brought to the attention of the Intergovernmental Forum on Chemical Safety by ILO.

ANNEX

Table 1: Proposal for definitions of gases, liquids and solids

Table 2: Proposal for hazard levels for the classification of flammable liquids

Table 3: Proposal for hazard levels for the classification of flammable solids

Table 4: Proposal for hazard levels for the classification of flammable gases

Table 5: Proposal for definition and criteria for the flammability of aerosols

Table 6: Proposal for tests and criteria for reactive substances

Table 7: Proposal for definitions for reactive properties

NOTES to Tables 6 and 7

Table 1: Proposal for definitions of gases, liquids and solids

Definitions	
Definition of gases and gas mixtures (substances, mixtures and solutions with a lower vapour pressure are regarded as liquids)	Vapour pressure at 50 °C > 300 kPa or completely gaseous at 20 °C (at standard pressure of 101.3 kPa)
Definition of liquids (substances not falling under this definition are regarded as solids)	Melting point ≤ 20 °C at 101.3 kPa or for viscous substances without a defined melting point, test according to ASTM D 4359-90 or penetrometer test as prescribed in Annex A.3 of the ADR*/ with penetrometer according to ISO 2137:1985

*/ European Agreement concerning the International Carriage of Dangerous Goods by Road (ECE/TRANS/115, United Nations publication Sales No. E.96-VIII-2).

Table 2: Proposal for hazard levels for the classification of flammable liquids

Level	Uniform hazard description	Characteristics	Testing methods
Very high danger	To be developed	Initial boiling point ≤ 35 °C and flashpoint < 23 °C	Closed cup methods to be used, open cup methods only acceptable in special cases (may be determined)
High danger	To be developed	Flashpoint < 23 °C and initial boiling point > 35 °C	
Medium danger	To be developed	Flashpoint ≥ 23 °C and ≤ 60 °C	
Low danger	To be developed	Flashpoint > 60 °C and ≤ 93 °C	

***Note**: Gas oils, diesel and light heating oils in the flashpoint range of 55 °C to 75 °C may be regarded as a special group for some regulatory purposes.*

Table 3: Proposal for hazard levels for the classification of flammable solids

Level	Uniform hazard description	Criteria	Testing methods
High danger	Not applicable	-	-
Medium danger	To be developed	Screening test: testing time 2 min (20 min for metal powders) Burning rate test: Substances other than metal powders: wetted zone does not stop fire and burning time < 45 s or burning rate > 2.2 mm/s Metal powders: burning time ≤ 5 min	Method as described in section 33.2.1 of the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria */
Low danger	To be developed	Method and test as described above Burning rate test Substances other than metal powders: wetted zone stops the fire for at least 4 minutes and burning rate < 45 s Metal powders : burning time > 5 min and ≤ 10 min	

*/ ST/SG/AC.10/11/Rev.2, United Nations publication sales No.E.95.VIII.2.

Table 4: Proposal for hazard levels for the classification of flammable gases

Level	Uniform hazard description	Characteristics and test methods
High danger	To be developed	Gases and gas mixtures, which at 20 °C and a standard pressure of 101.3 kPa, (a) are ignitable when in a mixture of 13 % or less by volume in air; or (b) have a flammable range with air of at least 12 percentage points regardless of the lower flammable limit. Flammability should be determined by tests or by calculation in accordance with methods adopted by ISO (see ISO 10156:1996). Where insufficient data are available to use these methods, tests by a comparable method recognized by the competent authority may be used.
Medium danger	To be developed	Gases or gas mixtures, other than those of high danger, which, at 20 °C and a standard pressure of 101.3 kPa, have a flammable range in mixture in air.
Low danger	Not applicable	Not applicable

***Note**: Ammonia and methyl bromide may be regarded as special cases for some regulatory purposes.*

Table 5: Proposal for definition and criteria for the flammability of aerosols

The working group on harmonized classification criteria for flammability agreed to include a definition and criteria for the flammability of aerosols in the proposal for the global harmonization. However technical discussions could not be finished and this issue will need further consideration.

TABLE 6 - TESTS AND CRITERIA for reactive substances				
HAZARD CATEGORY	**PHYSICAL STATE**	**PROPERTY**	**TESTS AND CRITERIA**	**COMMENTS**
Explosive	Solid or liquid	Explosibility Sensitiveness Thermal stability	According to UN test series 2 (Chapter 12)* According to UN test series 3 (Chapter 13) * According to UN test series 3(c) (Sub-section 13.6.1) *	Intentional explosives not subject to UN test series 2 UN transport system differentiates into subdivisions 1.1 to 1.4 and compatibility groups A to S to distinguish technical requirements
Organic peroxide	Solid or liquid	Oxidising Explosibility Sensitivity Thermal stability	1. The UN scheme, test series A to H (Part II of the Manual of Tests and Criteria) *, but sub-divisions may not be necessary for all systems. 2. Lower cut-off level was not agreed, and will need to be resolved.	The difference between the EU Supply side lower cut off value and that for the UN transport system needs further discussion.
Oxidising	Solid	Oxidising	UN Test 0.1 (Sub-section 34.4.1) *	
	Liquid	Oxidising	UN Test 0.2 (Sub-section 34.4.2) *	
	Gases	Oxidising	To be developed	Possibility of using ISO 10156. Further work on this is being carried out.
Pyrophoric	Solid	Pyrophoricity	UN Test N2 (Sub-section 33.3.1.4) *	
	Liquid	Pyrophoricity	UN Test N3 (Sub-section 33.3.1.5) *	

* Refer the Recommendations on the Transport of Dangerous Goods, Manual of Test and Criteria (ST/SG/AC.10/11/Rev.2, United Nations publication, Sales No. E.95.VIII.2).

TABLE 6 - TESTS AND CRITERIA for reactive substances				
HAZARD CATEGORY	**PHYSICAL STATE**	**PROPERTY**	**TESTS AND CRITERIA**	**COMMENTS**
Self-heating	Solid	Self-heating	UN Test N4 (Sub-section 33.3.1.6) *	Different hazard levels in UN Scheme.
Self-reactive	Solid or liquid	Explosibility Sensitivity Thermal stability	UN Test Series A to H (Part II of the Manual of Tests and Criteria) *	Systems not based on the UN should consider a separate classification for self-reactive substances.
Substances related to self-reactive substances and de-sensitised explosives.	Solid or liquid	Explosibility Sensitivity Thermal stability	To be based on UN tests *, but further discussion required.	1. Harmonisation should be based on UN but further improvements need to be discussed. 2. De-sensitised explosives should be a clearly identifiable category. Considerably more work required to resolve this issue.
React with water giving flammable gases.	Solid or liquid	Reactivity to produce flammable gas	UN Test N5. (Sub-section 33.4.1.4) *	Test N5 procedure amended slightly.
React with water giving toxic gases	Solid or liquid	Reactivity to produce toxic gas		Discussion started, but further information and work required.

* Refer the Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria (ST/SG/AC.10/11/Rev.2), United Nations publication, Sales number E.95.VIII.2).

Table 7: Proposal for definitions for reactive properties

HAZARD CATEGORY OR GROUP OF SUBSTANCES OR ARTICLES	PHYSICAL STATE	DEFINITION
Explosive	Solid or liquid	Solid or liquid substances (or mixtures of substances) which are in themselves capable by chemical reaction of producing gas at such a temperature and pressure and at such a speed as to cause damage to the surroundings, including pyrotechnic substances. Articles containing one or more explosive substances, except devices containing explosive substances in such quantity or of such a character that their inadvertent or accidental ignition shall not cause any effect external to the device either by projection, fire, smoke, heat or loud noise. Substances or articles which are manufactured with the view to producing a practical explosive or pyrotechnic effect; **Note**: a pyrotechnic substance is a substance or mixture of substances designed to produce an effect by heat, light, sound, gas or smoke or a combination of these as the result of non-detonative self-sustaining exothermic chemical reactions. Pyrotechnic substances are regarded as explosive substances even when they do not evolve gases.
Self-reactive	Solid or liquid	Thermally unstable substances liable to undergo a strongly exothermic decomposition even without participation of oxygen (air).(Excludes organic peroxides and substances which are explosive or oxidising.)
Pyrophoric	Solid or liquid	Substances which, even in small quantities, are liable to ignite within a short period of time after coming into contact with air.

HAZARD CATEGORY OR GROUP OF SUBSTANCES OR ARTICLES	PHYSICAL STATE	DEFINITION
Self-heating	Solid or liquid	Substances other than pyrophoric substances which, in contact with air and without energy supply, are liable to self-heating; these substances will ignite only when in large amounts and after long periods of time.
Oxidising	Solid or liquid	Substances which, while in themselves not necessarily combustible, may, generally by yielding oxygen, cause, or contribute to, the combustion of other material.
	Gaseous	Gases which may, generally by providing oxygen, cause, or contribute to, the combustion of other material more than air does.
Emission of flammable gases in contact with water	Solid or liquid	Substances which, by interaction with water, are liable to become spontaneously flammable or to give off flammable gases in dangerous quantities.
Organic peroxides	Solid or liquid	Organic substances which contain the bivalent - O-O - structure and may be considered derivates of hydrogen peroxide, where one or both of the hydrogen atoms have been replaced by organic radicals.
Substances related to self-reactives	Solid, liquid	No consensus reached, discussions not finished
De-sensitised explosives	Solid, liquid	No consensus reached, discussions not finished

***Note**: It has been suggested that ammonium nitrate and ammonium nitrate containing fertilizers represent a special case. Further discussion will be needed to reach a consensus.*

NOTES TO TABLES 6 AND 7

NOTE 1: It was recognised that the physical form in which a substance is tested can affect its classification. The UN tests are carried out in the form presented for transport, whereas other tests - especially for handling and use e.g. according to directive 67/548/EEC - may require grinding to a reference standard which gives better information on the comparative intrinsic properties of substances. Before this matter can be completely resolved further discussion is needed.

NOTE 2: Screening procedures should be developed and published as voluntary guidance to minimise the cost of testing products.

NOTE 3: The use of the word "explosive" can have different meanings and interpretation. Reference to "an explosive" or "explosives" is commonly understood to mean substances or articles in Class 1 of the UN scheme, that is those which are intentional explosives or have properties which when assessed under the UN procedure place them in Class 1. The description "explosive" can, however, be used to describe a property and as such it encompasses a wider range of substances than just those in Class 1, for example, substances related to self-reactive substances. The global harmonisation exercise requires that classification is based on intrinsic properties and the word 'explosive' in that context can be used to describe the property of a substance i.e. 'its ability to explode', as well as referring to a substance or article that has been designed to have explosive properties. This can lead to confusion and difficulty but in the above table 'explosive' refers to substances or articles which would be placed in Class 1 of the UN scheme.

Further discussion might be needed on if and how to distinguish between the explosive properties of substances and articles designed and manufactured for explosive effects and covered by class 1 of the UN Recommendations on the transport of dangerous goods and the intrinsic property of substances being able to explode, e.g. as further intrinsic property of certain self-reactive substances or certain organic peroxides.